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PLASMA TREATMENT OF GLASSES (A REVIEW)

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The use of plasma flame at different stages of glass production (synthesis, polishing, cutting, and decoration) is considered. The nature of the origin of gas inclusions in glass in treatment with nitrogen and argon plasma is investigated.

Plasma treatment of glasses is one of the most promising areas in contemporary glass production. Plasma flame can be used virtually in all technological stages of glass treatment. Plasma treatment of materials makes it possible to develop energy-saving and environmentally friendly technologies, shorten the production cycle, and improve the product quality.

The high temperatures of plasma make it possible to synthesize high-melting glasses. Thus, aluminum-yttrium glass was synthesized, whose composition (wt.%) was 43.7 yttrium oxide and 56.3 aluminum oxide. Such glass made in the form of glass balls with diameters 1100 – 2500 μm had a density of 4.08 – 4.12 g/cm^3 and a refractive index of 1.855. Several papers report the results of glass fiber production. Optical fiber was synthesized employing a plasma burner and taking silicon oxide powder as the initial material [2]. Optical fiber was synthesized in low-temperature plasma in the gaseous phase from halogens [3]. The high specific energy concentration in plasma jets made it possible to use them in polishing glass products. Good results were obtained in polishing household, crystal, and quartz glasses [4] with rotational speed of 30 – 45 min^{-1} and plasma flame treatment for 3 – 6 sec.

Quartz glass produced in nitrogen plasma based on the Verneille method had different parameters compared with the traditional gas-flame production method, in particular, light transmission and the temperature of the beginning of deformation (the latter decreased from 1490 to 1450°C) [5].

Plasma technology makes it possible to deposit technical-purpose coatings on glass products. Protective nickel oxide and aluminum oxide coatings on glass pipe surface were obtained using the method of plasma spray deposition [6].

Data on low-temperature plasma treatment of sheet glass edges are presented in [7]. The initial material was 5-mm glass preheated to 723 K.

Low-temperature plasma is used in hardening of various glasses [8]. Data on glass hardening through plasma radiation of the glass surface are given in [9]. Such hardening is the consequence of the incorporation of ions contained in plasma into the surface layer of glass. When glass in a melt is hardened by plasma heating, its surface becomes enriched with lithium cations [10].

In plasma cutting of soda lime glass, the latter was previously heated to 700 K. A grid of cracks is formed in the site of the thermal effect, with subsequent scaling of the glass to the depth of 100 – 400 μm. The fused zone exhibits cord-type structure and bubbles, which determines the emergence of thermal stresses of about 90 – 100 MPa in the surface layer [11]. As the consequence of plasma cutting, the remelted sheet glass zone constitutes 600 – 650 μm, whereas the zone containing bubbles 70 – 80 μm in diameter reaches 1500 μm. The condensate in the bubbles is represented by sulfur, sulfates, or metals making part of the glass composition. In some bubbles, cristobalite appeared, which facilitates crack formation [12]. In cutting quartz glass and soda lime glass in nitrogen plasma, bubbles are registered. In this case, under a high heating rate, the glass structure does not have time to relax, and the compounds constituting the glass decompose, which is accompanied by the formation of the gas phase. The processes of gas phase absorption and the release of physically soluble gases take place simultaneously [13].

In addition to the formation of a gas phase, the high-temperature effect can cause crystallization in the surface layers of glass, its rate and starting temperature depending on the impurity atom concentration [14]. The authors in [15] claim that the kind of plasma-forming gas has a significant effect on the emergence of bubbles in glass under plasma treatment. For instance, no bubbles are formed in the surface layer under treatment in argon plasma, whereas on replacing argon by nitrogen, a substantial amount of bubbles is formed.

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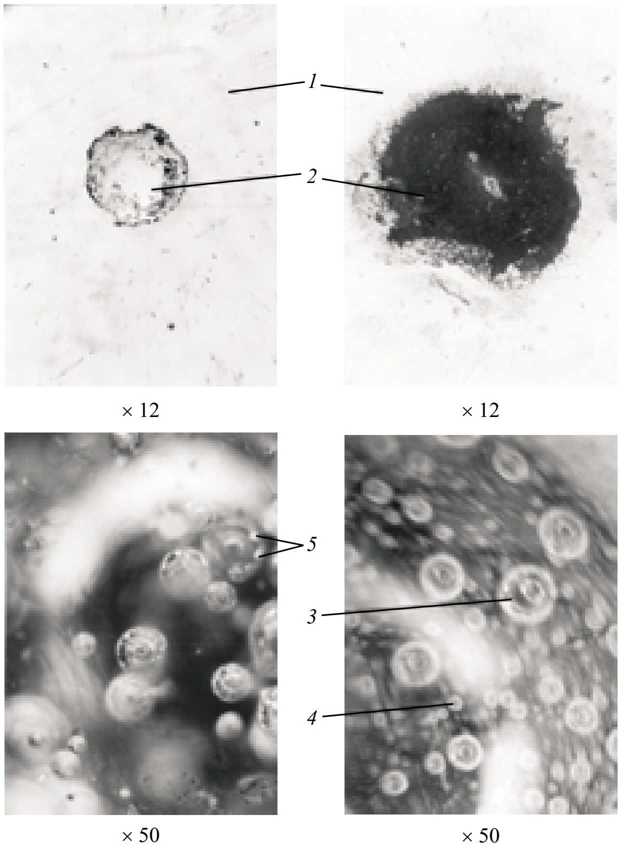

Fig. 1. Particles on milky and blue cobalt-tinted household glass deposited on sheet glass: *1*) substrate; *2*) deposited particle; *3*) gas inclusions with elements of devitrification; *4*) gas inclusions without devitrification elements; *5*) devitrification elements.

Additional decorative treatment of glass products substantially enhances their ornamental qualities. One of the most promising decoration methods consists in plasma spraying of glass powders with the grain size 80 – 250 μm on the surface of household glass [16]. A stencil was applied to articles preheated to 523 K, and glass powder was spray-deposited for 10 – 40 sec (depending on the surface area and the pattern configuration).

The samples of sheet, plate, figured, and reinforced glass were immobilized before the treatment started, and the plasma burner in the course of spray deposition of glass powder was moving at a speed of 10 – 15 cm/sec. The adhesive strength of such decorative coating to the substrate was 12 ± 1.5 MPa for the deposited layer thickness of 350 μm [17].

We carried out experiments in plasma spray deposition of glass on glass substrates. The substrate was sheet glass 4 and 5 mm thick produced by domestic glass manufacturers. The decorating materials were household glasses in the form of glass rods 0.8 – 2.5 mm in diameter produced at the Krasnyi Mai Glass Factory. The chemical compositions of the considered glasses are shown in Table 1.

The spray deposition was carried out employing a GN-5r plasma burner of an UPU-8M plasma gun. The plasma gun operating parameters were as follows: work voltage 30 V, current 350 A. The plasma-forming gas was argon with the flow rate 0.00114 g/sec at the pressure 0.25 MPa. The water consumed on chilling amounted to 0.6 m^3/h. The distance from the plasma burner nozzle to the glass substrate was 350 mm.

After plasma spray deposition, the optical spectroscopy method was used to study the reactions between the deposited particles and the substrate, as well as the bubbles arising both in the coating and in the substrate.

Figure 1 shows single deposited drops of milky and blue cobalt-tinted household glass.

In plasma spraying of decorative glasses, the sprayed particles in the plasma-forming gas flow had a shape close to a perfect sphere. The microscope studies identified gas inclusions 20 – 100 μm in diameter in the particles. Therefore, it can be stated that the material within the plasma flame becomes intensely heated in its entire volume. However, due to the shift of the equilibrium processes, relaxation in glass is not completed. Stabilization of glass particles through subsequent fast chilling does not occur. Therefore, one of the probable reasons for the formation of gas inclusions is the emission of gases that had been physically dissolved in the glass melt.

Since melted glass drops experience the high-temperature effect of plasma-forming gases, which at the exit from the plasma burner become mixed with air, the processes of reactions and dissolution of gases in sprayed particles may take place. This can be the second reason for the emergence of gas inclusions in the considered glasses.

TABLE 1

Glass*	Weight content, %										
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	ZnO	B_2O_3	Fe_2O_3	F
Household chromium-tinted green	72.7	–	6.8	2.0	15.0	2.0	0.5	–	1.0	0.05	–
Household cobalt-tinted blue	68.6	6.3	9.3	–	14.8	1.0	–	–	–	0.05	–
Milky	66.8	6.3	6.3	–	14.8	1.0	–	–	–	–	5.0
Household selenium ruby	66.5	1.0	–	–	13.0	6.0	0.4	8.0	3.5	0.05	–
Sheet	72.5	1.0	9.0	3.0	14.0	–	0.4	–	–	0.1	–

* Cr_2O_3 content in the household green glass was 1.0%, CoO content in the household blue glass was 0.002%, Cd and Se contents in the household selenium ruby glass was 0.5 and 0.5%, respectively.

It should be noted as well that certain components of glass may decompose under the effect of the high temperature of plasma. This is accompanied by the release of gas inclusions into the glass melt and can be the third reason for their emergence, which is substantiated by the fact that we could identify the products of devitrification on the internal sphere of the gas inclusions (Fig. 1).

The x-ray phase analysis made it possible to identify the specified phases, of which the main ones are quartz, cristobalite, and silicates and oxides of the metals that form part of the considered glass compositions.

Paper [18] supplies results of studying penetrability, diffusion, and solubility of inert gases, in particular, helium, both into monolithic glass and into glass containing sealed pores. The authors note that the process of helium penetration includes the stages of adsorption, physical dissolution, and diffusion, as well as surface desorption. It is observed that adsorption and dissolution of helium in glass proceed significantly faster than diffusion does. The authors conclude that the penetrability and diffusion coefficients in a monolithic membrane, in particular, in glass S87-1 of the platinum group, grow exponentially with increasing temperature [18].

Thus, it can be maintained that in our case argon dissolves in glass in the course of plasma spray deposition. This is corroborated by the fact that some of the gas inclusions do not contain devitrification products on their internal sphere. The microscopic studies established that gas inclusions with and without devitrification products are uniformly spread over the entire volume of the glass particle deposited on a glass substrate (Fig. 1).

In the course of plasma spraying, a melted glass particle contributes to the contact site an amount of heat sufficient for softening of the surface layer. This is corroborated by the gas inclusions identified in the surface layers of the glass substrate, which can be attributed to physically soluble gases. Figure 2 shows a crater in the surface layer of the glass substrate, which was formed as a consequence of tearing off a deposited drop when studying the strength parameters of the decorative coating. Gas inclusions 20 – 50 μm in diameter were registered along the entire perimeter of this crater.

Thus, plasma processes of synthesis, treatment, and decoration of glass and glass articles are increasingly used in the glass industry due to their advantages (economic efficiency, environmental safety, a shortened production cycle, etc.). Specifics of the plasma treatment of glass include the processes of partial devitrification both in nitrogen and argon plasma, as well as the release of physically dissolved gases into the glass volume in the form of bubbles.

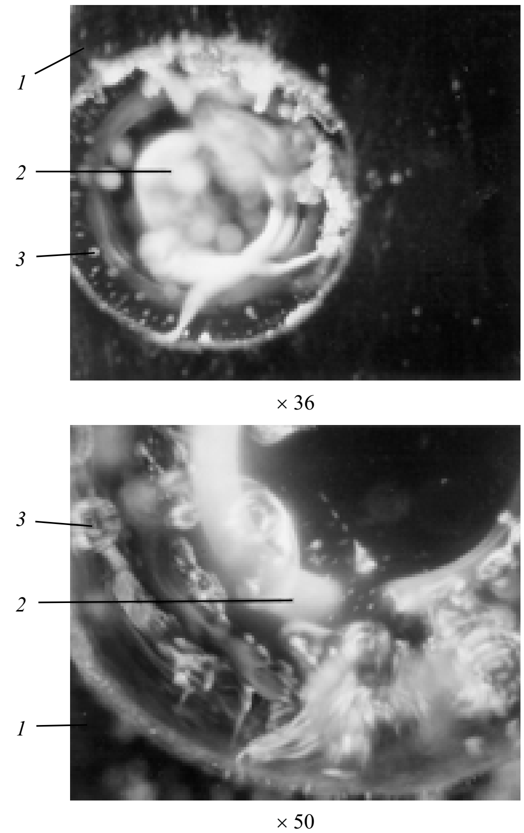

Fig. 2. A crater on sheet glass surface after tear-off of the deposited particle: *1*) substrate; *2*) crater; *3*) gas inclusions.

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